

KOKAI PATENT APPLICATION NO. HEI 3-152881

RECTANGULAR LITHIUM SECONDARY BATTERY

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RECTANGULAR LITHIUM SECONDARY BATTERY

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[There are no amendments to this patent.]

Specification

1. Title of the invention

Rectangular lithium secondary battery

2. Claims of the invention

(1) A battery comprising multiple positive electrodes, lithium negative electrodes, and an organic electrolyte arranged alternately inside a rectangular battery case, which rectangular lithium secondary battery is characterized by the fact that the area of each of the negative electrodes is greater than the area of the corresponding positive electrode, and the margin area of the negative electrode is located outside the margin area of the positive electrode.

(2) The rectangular lithium secondary battery described in Claim 1 wherein the number of negative electrodes is 1 more than the number of positive electrodes.

(3) The rectangular lithium secondary battery described in Claim 1 or Claim 2 wherein the active material of the positive electrodes is one or more materials selected from manganese dioxide, vanadium oxide, titanium dioxide, molybdenum sulfide, LiCoO_2 , and LiMn_2O_4 .

3. Detailed description of the invention

Field of industrial application

The present invention pertains to an organic electrolytic rectangular lithium secondary battery, and the invention further pertains to the structure of a rectangular lithium secondary battery.

Prior art

As a lithium primary battery having a high energy density, good storage stability, good autodischarge characteristics, and being leak-tight, graphite fluoride/lithium batteries, manganese dioxide/lithium batteries, thionyl chloride/lithium batteries, etc. are known and are in use.

Meanwhile, with the recent trend toward development of a reduced-size and portable electrical and electronic equipment, reduced-size and lightweight batteries are required for use as power sources, and due to the insufficient power capacity of conventional secondary batteries, great expectations are being placed on lithium secondary batteries as lithium batteries can be used repeatedly upon charging.

As a lithium secondary battery, a battery wherein molybdenum disulfide is used as the active material in the positive electrode is used in practice, and batteries where manganese dioxide, niobium selenide, etc. are used have been proposed.

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The major problem for practical application of lithium secondary batteries is the formation of a resinous lithium deposit (dendrite) on the negative electrode at the time of charging, resulting in an adverse effect on the charge and discharge of the battery, such as inactivation of the negative electrode and short-circuiting, so that an extended cycle life is not possible.

As factors in the formation of dendrite, 1. the degree of formation varies depending on the type of organic electrolyte used, 2. formation occurs when the charge density exceeds a certain value, 3. formation is likely to occur when a free electrolyte is present, 4. formation is likely to occur when the current density to the lithium negative electrode at the time of the charge is different, etc. can be mentioned.

As for the organic electrolyte, an adequate material can be produced when a suitable solvent and solute are used in combination. With regard to the charging current density, the problem can be solved when the electrode area is increased even though the energy density is

reduced. Furthermore, the free electrolyte can be managed through an increase in the precision of the battery structure and control of the amount of liquid. The point is how to stabilize the current distribution at the lithium negative electrode at the time of charging.

The current distribution in a strict sense is influenced by whether the surface conditions at the negative electrode are constant, correspond well with the positive electrode, firm adhesion with the separator exists, etc. For this reason, all lithium secondary batteries used in practice have a cylindrical structure where accurate layering of thin positive electrode and negative electrode plates having large areas is possible and winding under high tension is possible.

Problems to be solved by the invention

However, a battery shape that complies with the shape of the device is demanded by users. In other words, as the thickness and size of a device are reduced, smaller and thinner batteries are being demanded. In general, the shape of the device is rectangular, and in order to utilize the space in the device efficiently, a rectangular battery is required.

When a rectangular battery case is used, the following structures for the plates are conceivable: 1. a structure where long positive electrode plates and negative electrode plates such as those used for cylindrical batteries are wrapped via a separator and inserted into a battery case as [opposite sides of] the longitudinal face are being squeezed together; 2. a structure where plates are stacked via a separator and folded in an accordion fashion then inserted into the case; 3. a structure where one or both of the positive electrode and the negative electrode are cut to form a strip and wrapped with a separator, stacked alternately and inserted into the battery case, etc. However, when the electrode plate of 1 above is inserted into the case, formation of dendrite is likely to occur due to factors such as the degree of compression of the electrode varying on

each side of the case, and the state of liquid adsorption of the electrolyte by the plate varies, and furthermore, and the retention of liquid in the space inside the battery case, and, as a result, good charge-discharge cycle characteristics cannot be expected. In 2 above, where the folded plate is inserted to the battery case, the folds of the electrode are not uniform and uniform retention of the liquid is not likely to occur and the current density is likely to vary compared to other areas, and dendrite is likely to form as well; thus, good charge-discharge cycle characteristics cannot be expected. It is therefore necessary to use for a structure of the rectangular lithium secondary battery to have a structure where electrode strips are stacked and the tension of the electrodes is increased. A state where the degree of tension is high or the structure of the electrode is neat is technically possible, but a problem does exist in this case, as well. Namely, when the current distribution varies on the lithium negative electrode at the time of charging, formation of dendrite is likely to occur, but it can be assumed that the current distribution remains constant in the areas where the positive electrode and negative electrode are in correspondence. Therefore, the area where nonuniform current is likely to occur is at the ends, that is, the margins, of the electrode. The margin areas of the long electrodes used in cylindrical batteries are relatively constant and the area is limited, but when strip-like electrodes are used in a rectangular battery, the electrode itself is small and many pieces are used, thus many margin areas exist. As a result, dendrite is likely to form and the charge-discharge cycle characteristics are likely to be inadequate.

Means to solve the problem

The present invention aims at eliminating the above-mentioned problems, and producing a rectangular lithium secondary battery that is characterized by the fact that the area of each negative electrode is greater than the area of the corresponding positive electrode, and the

marginal member of the negative electrode is located outside the margin area of the positive electrode in a battery comprising multiple positive electrodes, lithium negative electrodes, and an organic electrolyte arranged alternately inside a rectangular battery case.

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Work of the invention

In a lithium secondary battery, it is necessary to prevent formation of dendrite at the time of charging the battery to achieve adequate charge-discharge cycle characteristics. When the above-mentioned short strip electrode is used, formation of dendrite is likely to occur at the margin area of the lithium negative electrode. In other words, when the negative electrode and positive electrode strips are arranged via a separator, the distance from the corresponding positive electrode remains constant in the center area of the negative electrodes, and the current density at the time of charging becomes constant as well. On the other hand, many small positive electrodes and negative electrodes strips are stacked, and as a result, the possibility of the end members of the positive electrodes sticking out beyond the end members of the negative electrodes exists. In this case, the distance between the end members of the negative electrodes is closer to the positive electrodes; thus, that area undergoes priority reaction with the positive electrode, and formation of dendrite is likely to occur and the charge discharge cycle life is reduced.

Based on the above background, the area of the negative electrodes is increased compared to the corresponding area of the positive electrodes in the present invention, and formation of dendrite is prevented by avoiding gaps in the overlapping of the positive electrodes and negative electrodes, and even when gaps do exist, the positive electrode is prevented from sticking out

beyond the negative electrode so that production of a rectangular lithium secondary battery having good charge-discharge cycle characteristics is possible. In this case, priority reaction of the negative electrode with the closest positive electrode is utilized, and when many positive electrodes and negative electrodes are stacked and the positive electrodes are placed at the outside, it is necessary to control the thickness of the positive electrodes on the outer-most side to 1/2 or less of the thickness of the positive electrodes on the inner side to prevent an increase in the current density of the corresponding negative electrodes since the reaction of the positive electrodes increases with an increase in the thickness of the positive electrodes to a certain point, and use of a positive electrode with a different thickness in the same battery poses a problem from the standpoint of production; furthermore, in the case of a lithium negative electrode, a reduction in the current density does not pose a problem; thus, when short, strip-like electrodes are stacked and used in a rectangular lithium secondary battery, it is desirable when the negative electrode is located on the outer-most side. The invention is further explained in detail with the application example below.

Application example

Fig. 1 is a structural drawing of the battery of an application example of the present invention. In Fig. 1, 1 is a negative electrode plate, and an aqueous dispersion of manganese dioxide used as the active material of the positive electrode, an electro-conductive carbon powder, and polyethylene tetrafluoride, that serves as a binder, were mixed at weight ratios of 100:7:7 and formed into a paste, the mixture was coated onto both surfaces of an aluminum foil with a thickness of 30 μm , dried, and rolled and cut to the specified dimensions. Among the

above-mentioned materials, the weight ratio of the polyethylene tetrafluoride is calculated in terms of the solid component in the dispersion. Furthermore, the size of the electrode was 12.5 x 48 mm and the thickness was 0.3 mm. Assuming that the manganese dioxide undergoes a monovalent reaction, the theoretical charge quantity of electricity is 120 mAh. 2 is a separator and is a porous polypropylene film. 3 is the lithium negative electrode, and the size is 14 x 50 mm, and the thickness is 0.18 mm. The theoretical charge quantity of electricity per negative electrode is 250 mAh. Five positive electrodes and 6 negative electrodes were used to produce the positive electrode and negative electrode structure; thus, 600 mAh for the positive electrodes and 1500 mAh for negative electrodes are achieved in the overall battery, and one side alone undergoes a reaction in the lithium located at the outer-most side; thus, 1250 mAh is achieved. Furthermore, the actual charge and discharge [reaction] of the positive electrode is approximately 0.4 valent. The above-mentioned electrode component is inserted to a battery case 8 made of an iron-nickel plating having an insulation sheet 10 made of polypropylene at the bottom; then, spot welding the titanium leads 4 from each of the positive electrodes to hermetic terminal 7 imbedded in stainless steel seal plate 5 via glass seal 6. Furthermore, the nickel negative electrode leads from each negative electrode are formed into a bundle and spot welded to case 8. After the above-mentioned processes were completed, an electrolyte prepared by dissolving lithium hexafluorophosphate (LiPF_6) in propylene carbonate at a ratio of 1 mole/l was injected, and seal plate 5 was inserted into case 8, and laser welded to produce the battery. The finished size of the resulting battery was 4x16x60 mm with the exception of the positive electrode terminal member. The battery produced is defined as battery A.

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Fig. 2 shows a battery made of the same materials, and the battery structure and production method are the same as those of battery A above; the size of the positive electrode plates alone was changed to 14x50 mm, which is the same size used for the negative electrodes. The thickness was 0.3 mm, which is the same as in battery A. Thus, the theoretical charge quantity of electricity of the positive electrodes becomes higher than that of battery A, and a reaction of the overall battery of 670 mAh was achieved. The battery produced is defined as battery B.

Fig. 3 shows a battery where the size of the positive electrodes and negative electrodes are the same as in battery B but the structure of the battery is reversed from that of battery A or B. In other words, as shown in Fig. 3, the positive electrode is the outer most of the group of plates, and as a result, 6 positive electrodes and 5 negative electrodes are used. The theoretical charge quantity of electricity for the positive electrodes was 800 mAh and that of negative electrodes was 1250 mAh. In this case, assuming that only one side of each of the two positive electrodes on the outer-most side function, the charge quantity of electricity for the positive electrode becomes 670 mAh. The battery produced is defined as battery C. For the batteries produced above, a charge-discharge cycles of 3.8 V at a charge current of 20 mA to 2.0 V at a discharge current of 60 mA were repeated at a temperature of 20°C. The relationship between the discharge capacity and the number of cycles is shown in Fig. 4. As shown in Fig. 4, battery A of the present invention exhibits excellent charge-discharge cycle characteristics. On the other hand, a higher discharge capacity is observed in battery B and battery C in comparison to battery A, but fluctuation in the discharge capacity is observed at approximately 80 cycles in battery B and at approximately 50 cycles in battery C, and charge and discharge are impossible from that

point on. When the above-mentioned batteries were disassembled and examined, formation of dendrite was observed in battery B and battery C in the margin areas of the negative electrodes, and short-circuiting of the battery occurred as a result. The above-mentioned phenomenon was clearly observed for the negative electrodes on the outer-most side as well in battery C. On the other hand, formation of dendrite was hardly observed in battery A. Therefore, the reason for reduction in capacity observed in battery A at approximately 250 cycles was not caused a result of short-circuiting of the battery, but the charge and discharge efficiency of the lithium negative electrode is approximately 98% in the system.

Effect of the invention

As explained in detail above, according to the present invention, formation of dendrite on the lithium negative electrode can be controlled and a rectangular lithium secondary battery having good charge-discharge cycle characteristics can be produced when a short strip-like electrode is used in a rectangular lithium secondary battery, and the positive electrodes and negative electrodes have a structure such that the margin area of the lithium negative electrodes is located on the outer side of the corresponding positive electrode so as to form a charge current on the lithium negative electrodes corresponding to the positive electrode at the time of charging of the battery and to form a current on the lithium electrode located at the outer side of the positive electrodes below the above-mentioned current. It should be noted that the effect achieved above is based on the structure of the positive electrodes and negative electrodes, and the effect is not limited to the positive electrodes used in combination with the lithium negative electrodes, but needless to say, a material having good chemical stability is desired for the positive electrode active material, and for example, a material selected from manganese dioxide,

vanadium oxide, titanium dioxide, molybdenum sulfide, LiCoO_2 , and LiMn_2O_4 can be used effectively.

4. Brief description of figures

Fig. 1 is a cross-section view that shows the structure of the battery of an application example of the present invention, Fig. 2 and Fig. 3 are cross-section views used for comparison, and Fig. 4 shows the relationship between the discharge capacity and number of cycles.

Explanation of codes

1 ... Positive electrode plate, 2 ... Separator, 3 ... Negative electrode plate, 4 ... Positive electrode lead, 5 ... Seal plate, 6 ... Glass seal, 7 ... Positive electrode terminal, 8 ... Battery case, 9 ... Negative electrodes lead, 10 ... Insulation plate

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and 1 other

[p. 5]

1 ... Positive electrodes plate

2 ... Separator

3 ... Negative electrodes plate

4 ... Positive electrodes lead

5 ... Seal plate

6 ... Glass seal

7 ... Positive electrode terminal

8 ... Battery case

9 ... Negative electrode lead

10 ... Insulation plate

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Fig. 1

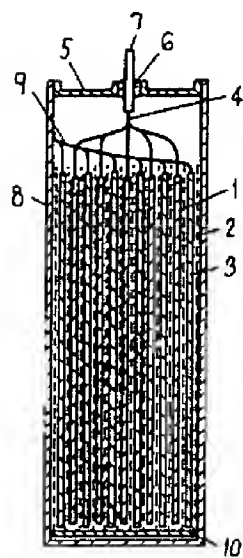


Fig. 2

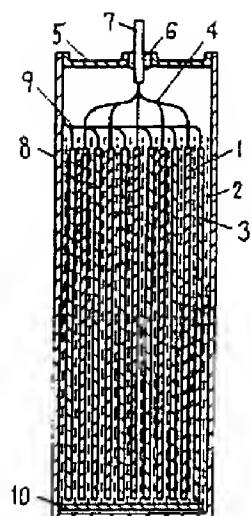


Fig. 3

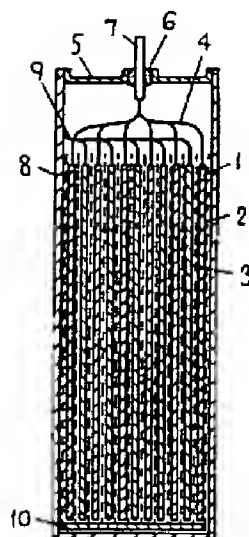
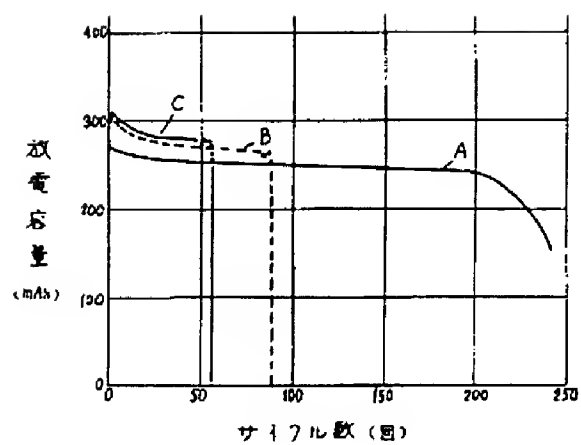


Fig. 4



Vertical axis: discharge capacity (mAh)

Horizontal axis: cycle number (number of times)